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PRELIMINARY INVESTIGATION OF PHENOLIC CONTAMINATION OF SAMPLES BY FIELD AUTOSAMPLERS

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ABSTRACT

Ontario Hydro reported that the peristaltic pump automatic wastewater samplers they used for 24 hour composite samples could contaminate water samples with reactive phenolics measured by the 4-AAP test (MISA analytical test group 14). Our brief investigation showed that phenolics-free distilled deionized water (buffered to pH 7) collected as a 24 hour composite sample by American Sigma samplers (model 706) contained up to 5 µg/L of phenolics, as phenol. The investigation further showed that water stored inside surgical grade silicone pump tubing and in contact with the wetted surface of sampler liquid sensors for 24 hours showed phenolic contamination levels of up to 47 µg/L as phenol. Although the silicone tubing proved to be a major source of reactive phenolics, actual sample contamination under field sampling conditions will depend on many factors. Neither these factors, nor alternative samplers or pump tubing were investigated. Instead we recommend that users demonstrate that field sampling devices/techniques neither add nor remove the analyte of interest. A suitable demonstration would be the sampling and analysis of blanks and spiked blanks for reactive phenolics, whenever a new or altered sampler is to be used, and the verification of findings annually thereafter. Finally, reactive phenolic results, up to 5 µg/L as phenol, from 24 hour composite samples collected by autosamplers using silicone tubing, should not be considered as distinguishable from sample blanks.

INTRODUCTION

MISA monitoring regulations allowed the use of field autosamplers for the collection of samples for the reactive phenolics 4-AAP test (MISA analytical test group 14). Ontario Hydro reported to the MISA Joint Analytical Working Group that peristaltic pump type automatic wastewater samplers, employing surgical grade silicone pump tubing, referred to as autosamplers herein, could contaminate water samples with reactive phenolics, the analyte of interest (Otto Herrmann, pers. comm.). Environment Ontario undertook an investigation into contamination from its autosamplers, to see if alternative sampling procedures were necessary for ATG 14.

The MISA monitoring regulation specified that the sample should not contact any material other than glass, stainless steel, Teflon®, or surgical grade silicone tubing during collection. The source of contamination reported by Ontario Hydro was unknown, but suspected to be through the silicone tubing. The approach of the investigation was to evaluate the levels of contamination possible from the autosamplers, under controlled laboratory conditions, and then to test the sampler's various contact surfaces to determine the source(s) of contamination.

PROCEDURE

Pre-test Cleaning

Before each test was conducted, the tubing loops were cleaned by Central Stores Staff of the Laboratory Services Branch. The cleaning consisted of recirculating Methanol followed by distilled water through the loop for 30 minutes each.

All of the automatic sampler bottles used were also cleaned by Central Stores Staff. This consisted of bottle washing, in an industrial dishwasher, than oven baking for four hours.

Phase One: Recirculation and Sampling

The goal of phase one was to evaluate, under controlled laboratory conditions, the level to which field autosamplers can contaminate samples with reactive phenolics.

Two American Sigma model 706 field autosamplers were placed together on a laboratory bench, but operated independently (Fig.1). Phenolics-free water samples were analyzed after continuous recirculation through the samplers pumping system for 24 h. In a subsequent test, phenolics-free water samples were analyzed after sampling over 24 h at 15 min. intervals (19 mL/interval, pumping forward time = 4 sec.) using the MISA time proportional composite sampling protocol (Fig.2.).

Under the MISA monitoring phase, automatic sampling devices could be used that collected and combined equal volume sub-samples at time intervals not exceeding fifteen minutes, during an operating day (24 hour period). At the end of the operating day the time proportional composite sample collected would be analyzed for various test groups. Some of the analytical test groups monitored, required dedicated sample jars and could not be taken from the composite collected. Therefore the automatic samplers were programmed to collect more than one composite sample over an operating day, commonly known as a multi-bottle composite. In the most common automatic samplers up to eight multi-bottle composites can be collected throughout an operating day.

The automatic samplers used in this investigation were programmed to collect two bottle composites (bottle #1, 2 for each automatic sampler) over a twenty-four period. The 24 h composite sampling test was repeated two weeks later.

The autosamplers wetted contact surfaces included the Teflon® lined polyethylene tubing, which will herein be referred to as Teflon® tubing, (intake line) connecting each sample "source" flask to each sampler, and surgical grade silicone tubing in the sampler, and the sampler liquid sensor. Controls consisted of manual grab samples (250 mL) pumped through the autosampler directly into sample bottles immediately before starting the recirculation experiment and before the start of the 24 h composite sampling during week two. A control flask of water containing ends of a loop of Teflon® tubing was placed between the sampling source flasks. Samples were collected in sample containers, precharged with 10 N sulphuric acid (about 4 mL of acid/L). The samples collected during the 24 h composite by the autosampler were split and analyzed in duplicate.

Phase Two: Contact Surfaces Testing

Since phase one showed that field autosamplers could contaminate samples* with reactive phenolics, to a significant level, the goal of phase two was to determine the source of the contamination. Phenolics-free water was analyzed after exposure for 24 hours inside tubing loops.

The sampling loops studied consisted of the wetted contact surfaces of the autosamplers, individually and in various combinations, independent of the autosamplers. The contact surfaces are; three foot sections of surgical grade silicone tubing, five foot sections of Teflon® tubing and the liquid sensor. The autosampler's liquid sensor is made up of two sections of stainless steel tubing (1.25" and 2.5") connected by a 3/8" section of silicone tubing. A 2" section of surgical grade silicone tubing was used to connect the teflon® lined polyethylene tubing to the liquid sensor. Control flasks, one covered with foil and another open to atmosphere were placed in the area where the tubing was tested.

* The 24 hour composite testing was repeated in this phase.

RESULTS

Sampling Effects

Results from recycling and MISA composite sampling phase (one) are shown in Table 1.

The initial blank results (samples #1, 23) at 1.1 and 0.3 µg/L as phenol were not analytically different from the ambient blanks (samples #4, 26) and grab results (samples #2, 3, 24, 25) ranging from 0.8 to 1.1 µg/L as phenol. Blank water recirculated for 24 h (samples #5, 6) showed higher contamination at 7.1 to 7.6 µg/L as phenol, while simulated MISA composite sampling over 24 hours (samples #7 - 14 and 15 - 22) resulted in lower, but analytically significant contamination, from 1 to 4.8 µg/L as phenol.

Results from MISA composite sampling, repeated in phase two are shown in Table 2.

Again, blank results were universally low (samples #101, 104, 105, 108, 109): from 0.3 to 0.4 µg/L as phenol. Grab samples collected through the samplers (samples #102, 103, 106, 107) were slightly higher, but not analytically different: from 0.4 to 0.6 µg/L as phenol. MISA composite samples over 24 hours (samples #111 to 118) again resulted in higher contamination: from 1 to 2.4 µg/L as phenol.

Contact Surface Effects

With data showing that field auto samplers could contaminate samples with reactive phenolics to a significant degree, the study focused on the wetted contact surfaces. Results are shown in Tables 3, 4, and 5.

The blank water stored 24 h in the loop consisting of all wetted contact surfaces joined together (sample #110), gave the highest result so far: 24.5 µg/L as phenol; more than ten times the MISA monitoring regulation method detection limit (MDL) set at 2 µg/L as phenol.

Further data, shown in Table 3, showed no contamination in controls (samples #201 to 204, and 208, 209): from 0.2 to 0.5 µg/L as phenol. Samples from loops of the same components as sample #110 (samples # 205 to 207) showed levels of contamination similar to those for #110: from 26.3 to 30.9 µg/L as phenol.

A second tubing study, for which data is shown in Table 4, compared contamination from a variety of tubing combinations. Controls again were found uncontaminated (samples #301 to 304, 315, 316): from 0.2 to 0.3 µg/L as phenol. Loops similar (samples # 313, 314) to those used above showed contamination of 17.8 and 19.8 µg/L as phenol. The Teflon®/silicone combination (samples #311, 312) gave similar results: 19.9 to 21.7 µg/L as phenol. Water from silicone-only tubing loops (samples #307 to 310) showed the highest contaminated: from 37.9 to 38.3 µg/L as phenol. A GC/mass spectrometer

analysis of one of these samples gave an estimate of 33 µg/L of pure phenol.

A third tubing study, results shown in Table 5, was made to confirm contamination potential of different brands of silicone tubing. Two sets of silicone tubes were tested:

1. Surgical Grade tubing purchased through Fred A. Dungey Inc. (cat. #PTS098) (a) new from the package and (b) washed with alcohol and distilled water.

2. Surgical Grade tubing from Dow Corning (Silastic Medical grade, cat. #601) (a) new from the package or (b) washed with alcohol and distilled water.

In addition, two sets of three liquid sensors connected in series with short pieces of Teflon® tubing were tested for contamination potential.

All controls showed less than 0.4 µg/L as phenol (samples #401 to 406, #415, 416). Liquid sensor loops had phenolic levels of 13.8, 13.9 µg/L as phenol (samples #417, 418). All the silicone tubing loops had similar, elevated phenolic concentrations: 43.2 to 46.6 µg/L as phenol. A GC/mass spectrometric analysis of one of these samples showed pure phenol as the predominant contaminant, at about 10 µg/L as phenol.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Reactive phenolics contamination can occur in field autosamplers that use surgical/medical grade silicone tubing. Factors which determine the extent of contamination have not been investigated. These would likely include exposure time, ratio of exposed area to sample volume, temperature and sample pH. Other components of autosamplers may contribute to the contamination of samples, but these were not investigated in this study. Hence our conclusions and recommendations concentrate on present findings and practical solutions that can be applied now.

In general, blank samples in the laboratory did not show phenolic contamination, nor did pumped grab samples, nor did blank water stored inside Teflon® tubing for 24 hours.

Measurable contamination was found under the following circumstances, in increasing order: 24 hour composite samples (1-4.8 µg/L as phenol), 24 hour recirculated water (7.1 to 7.6 µg/L as phenol), 24 hour exposure inside various tubing combinations (17.8 to 30.9 µg/L as phenol), and finally 24 hour exposure inside surgical grade silicone tubing (37.9 to 46.6 µg/L as phenol). The main conclusion is that exposure of samples to silicone rubber tubing causes phenolic contamination.

Under ideal sampling conditions, such as the pumped grab samples in the laboratory, contamination was unmeasurable. If samples making up a composite sample were collected like the grab samples, then no contamination should be measured. However, contamination was found in the 24 hour composite samples, collected by the autosampler (MISA protocol). The lines may not have been cleared as well as expected between samples, or the small film of water left in the pump tubing between samples may have extracted sufficient phenolics thereby contaminated aliquots collected for the composite.

Recommendations

1. Reactive phenolics 4-AAP (MISA ATG 14) results should be interpreted with caution whenever field autosamplers have been used to collect composite samples, and particularly when the samplers used silicone tubing. In the latter case, reactive phenolic results up to 5 µg/L should be not be considered distinguishable from a blank sample (i.e. not considered a positive result). This must be considered when examining data which were collected during the MISA monitoring phase.

2. Users should demonstrate that field sampling devices/techniques neither add nor remove reactive phenolics measured by the 4-AAP test (MISA ATG 14).

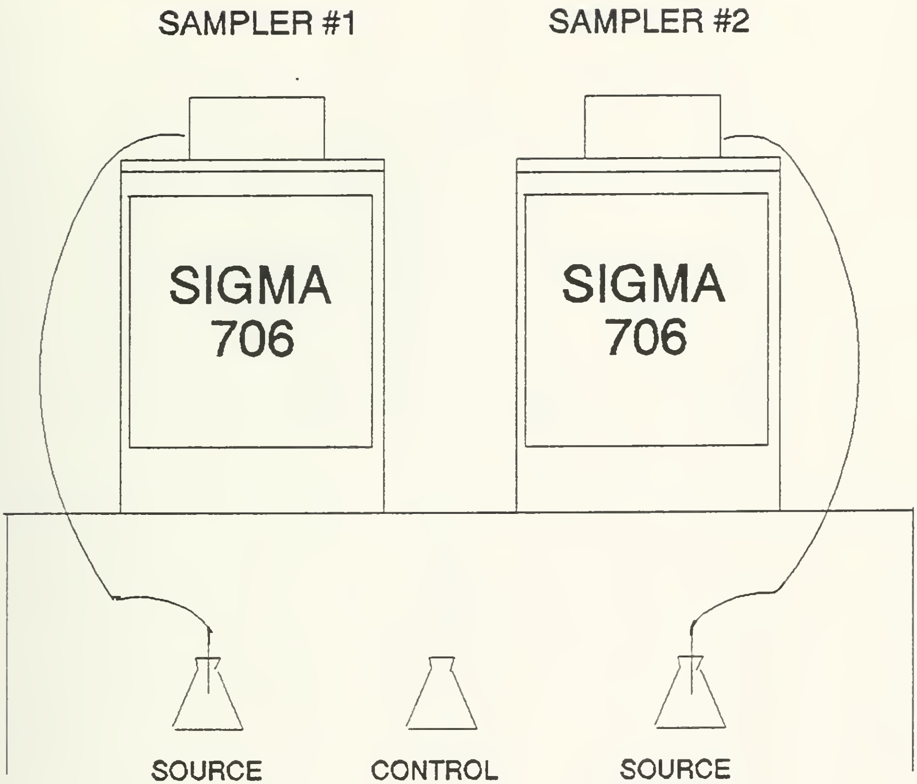
    2.1 Users should sample and analyse blanks and spiked blanks for reactive phenolics whenever a new autosampler is put into use, and annually thereafter. These check samples should be collected using the same procedure as for regular samples. It may be useful to collect phenolics samples last in the autosampler sequence; contamination may decrease toward the latter samples, due to rinsing. This should be tested with check samples.

    2.2 Check samples should also be collected whenever new or untested materials/sampling techniques (including manual grab) are used.

    2.3 Records of check sample results should be kept in a log book that is available for inspection.

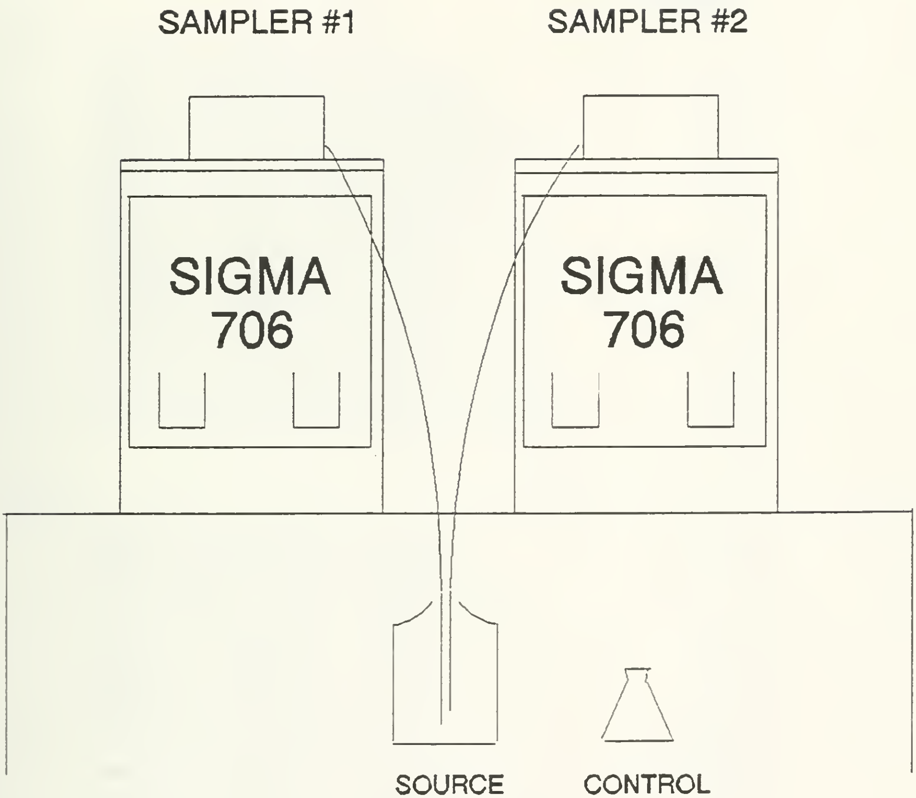
    2.4 Whenever the above conditions cannot be met, manual grab samples only should be collected with proven equipment (e.g. stainless steel bucket). If silicone tubing is employed, it should be rinsed with sample (pumped) for 30 seconds before collecting the sample. Practicality suggests that consideration should be given to allowing the MANUAL 3 composite sampling technique* for reactive phenolics by 4-AAP (MISA ATG 14).

* MISA protocol document subsect 2.2.2 (composite; 3 grabs/24 hours; 6 hours apart)



RECIRCULATION

FIGURE 1



COMPOSITE SAMPLE

FIGURE 2

TABLE 1

SAMPLE #	DESCRIPTION	RESULT (ppb phenol)
WEEK #1		
1	CONTROL FLASK, INITIAL BLANK	1.1
2	MANUAL GRAB THROUGH SAMPLER #1	0.9
3	MANUAL GRAB THROUGH SAMPLER #2	0.8
4	CONTROL FLASK, 24 HOUR, AMBIENT BLANK	0.4
5	SAMPLER #1, 24 HOUR RECIRCULATED	7.6
6	SAMPLER #2, 24 HOUR RECIRCULATED	7.1
7	SAMPLER #1, BOTTLE #1, 24 HOUR	3.9
8	SAMPLER #1, BOTTLE #1, 24 HOUR,DUPLICATE	4.2
9	SAMPLER #1, BOTTLE #2, 24 HOUR	3.5
10	SAMPLER #1, BOTTLE #2, 24 HOUR,DUPLICATE	2.4
11	SAMPLER #2, BOTTLE #1, 24 HOUR	4.8
12	SAMPLER #2, BOTTLE #1, 24 HOUR,DUPLICATE	4.5
13	SAMPLER #2, BOTTLE #2, 24 HOUR	4.5
14	SAMPLER #2, BOTTLE #2, 24 HOUR,DUPLICATE	4
WEEK #2		
23	SOURCE FLASK, INITIAL BLANK	0.3
24	MANUAL GRAB THROUGH SAMPLER #1	0.9
25	MANUAL GRAB THROUGH SAMPLER #2	1
26	SOURCE FLASK, 24 HOUR, AMBIENT BLANK	1.1
15	SAMPLER #1, BOTTLE #1, 24 HOUR	2.9
16	SAMPLER #1, BOTTLE #1, 24 HOUR,DUPLICATE	2.9
17	SAMPLER #1, BOTTLE #2, 24 HOUR	2.2
18	SAMPLER #1, BOTTLE #2, 24 HOUR,DUPLICATE	1.9
19	SAMPLER #2, BOTTLE #1, 24 HOUR	2.5
20	SAMPLER #2, BOTTLE #1, 24 HOUR,DUPLICATE	1.9
21	SAMPLER #2, BOTTLE #2, 24 HOUR	1
22	SAMPLER #2, BOTTLE #2, 24 HOUR,DUPLICATE	1.7

TABLE 2

SAMPLE #	DESCRIPTION	RESULT (ppb phenol)
101	SOURCE FLASK, INITIAL BLANK	0.4
102	MANUAL GRAB THROUGH SAMPLER #1	0.4
103	MANUAL GRAB THROUGH SAMPLER #2	0.5
104	CONTROL FLASK, INITIAL BLANK	0.2
105	SOURCE FLASK FOR TUBING, BLANK	0.4
106	SAMPLER #1, MANUAL GRAB, 24 HOUR	0.6
107	SAMPLER #2, MANUAL GRAB, 24 HOUR	0.5
108	CONTROL FLASK, 24 HOUR, AMBIENT BLANK	0.3
109	SOURCE FLASK, 24 HOUR, AMBIENT BLANK	0.4
110	TUBING, 24 HOUR	24.5
111	SAMPLER #1, BOTTLE #1, 24 HOUR	2
112	SAMPLER #1, BOTTLE #1, 24 HOUR,DUPLICATE	1.4
113	SAMPLER #1, BOTTLE #2, 24 HOUR	1
114	SAMPLER #1, BOTTLE #2, 24 HOUR,DUPLICATE	1.1
115	SAMPLER #2, BOTTLE #1, 24 HOUR	2.4
116	SAMPLER #2, BOTTLE #1, 24 HOUR,DUPLICATE	2.3
117	SAMPLER #2, BOTTLE #2, 24 HOUR	1.9
118	SAMPLER #2, BOTTLE #2, 24 HOUR,DUPLICATE	1.7

TABLE 3

SAMPLE #	DESCRIPTION	RESULT (ppb phenol)
201	SOURCE FLASK FOR TUBING #1, BLANK	0.2
202	SOURCE FLASK FOR TUBING #2, BLANK	0.2
203	SOURCE FLASK FOR TUBING #3, BLANK	0.2
204	CONTROL FLASK CLOSED, BLANK	0.3
205	TUBING LOOP #1, 24 HOUR	26.3
206	TUBING LOOP #2, 24 HOUR	29.3
207	TUBING LOOP #3, 24 HOUR	30.9
208	CONTROL FLASK CLOSED, 24 HOUR	0.4
209	CONTROL FLASK OPEN, 24 HOUR	0.5

NOTE: SAMPLE # 203 ALSO SERVES AS THE CONTROL FLASK OPEN, BLANK

TABLE 4

SAMPLE #	DESCRIPTION	RESULT (ppb phenol)
301	FLASK USED FOR TUBING FILL, BLANK	0.2
302	CONTROL FLASK OPEN, BLANK	0.2
303	CONTROL FLASK CLOSED, BLANK	0.2
304	LARGE FLASK, BLANK	0.3
305	5'TEFLON, 24 HOUR	0.2
306	5'TEFLON, 24 HOUR	0.2
307	3' SILICONE, 24 HOUR	38.3
308	3' SILICONE, 24 HOUR	38.3
309	3' SILICONE, 24 HOUR	38.1
310	3' SILICONE, 24 HOUR	37.9
311	TEFLON/SILICONE, 24 HOUR	19.9
312	TEFLON/SILICONE, 24 HOUR	21.7
313	TEFLON/SILICONE/LIQUID SENSOR, 24 HOUR.	19.8
314	TEFLON/SILICONE/LIQUID SENSOR, 24 HOUR.	17.8
315	CONTROL FLASK OPEN, 24 HOUR	0.2
316	CONTROL FLASK CLOSED, 24 HOUR	0.2

TABLE 5

SAMPLE #	DESCRIPTION	RESULT (ppb phenol)
401	LARGE FLASK, BLANK	0.2
402	FLASK USED FOR TUBING FILL, BLANK	0.2
403	LARGE FLASK, BLANK, LOW VOL	0.2
404	FLASK BLANK, HIGH VOL	0.2
405	CONTROL FLASK OPEN, BLANK	0.2
406	CONTROL FLASK CLOSED, BLANK	0.2
407	DOW1 TUBING, NOT WASHED, 24 HOUR	45.6
408	DOW2 TUBING, NOT WASHED, 24 HOUR	43.8
409	W.DOW1 TUBING, WASHED, 24 HOUR	46.6
410	W.DOW2 TUBING, WASHED, 24 HOUR	45.2
411	STORE1 TUBING, NOT WASHED, 24 HOUR	45.4
412	STORE2 TUBING, NOT WASHED, 24 HOUR	46.2
413	W.STORE1 TUBING, WASHED, 24 HOUR	43.2
414	W.STORE2 TUBING, WASHED, 24 HOUR	44.6
415	CONTROL FLASK OPEN, 24 HOUR	0.4
416	CONTROL FLASK CLOSED, 24 HOUR	0.2
417	#1 LIQUID SENSORS (3), 24 HOUR	13.8
418	#2 LIQUID SENSORS (3), 24 HOUR	13.9

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